where constant currents are wanted for a longer period, the working of a number of elements or batteries connected by means of a commutator in such a way that one element or battery will always be out of the circuit, and have its gases changed, and be replaced in the circuit at the moment when the next element or battery is switched out for the same purpose.

In using, in place of sulphuric acid, a solution of sodium chloride as electrolyte, we found, after working the battery for some time, sodium hydrate on one side and HCl on the other side of the battery, and have been able to determine in this case the polarisation to be equal to 0·54 volt, which very nearly accounts for the difference between the E.M.F. of the open battery and the E.M.F. calculated according to Thomson's theorem. The E.M.F. of PtH,NaClAq,PtO we found equal 0·86 volt, which, added to the polarisation of 0·54 volt just mentioned, gives a total of 1·40 against the theoretical figure for H, O = 1·47. By changing the gases after the polarisation was fully established, the battery showed an E.M.F. of 1·39 volts.

This observation, as well as the determinations of Peirce,[*] of the E.M.F. of gas batteries with the same gases and different electrolytes, shows that the electrolyte also has considerable influence upon the E.M.F.

We hope by further investigation to arrive at assigning their proper value to the various causes affecting the E.M.F. of gas batteries.

VI. "Contributions to the Chemistry of Storage Batteries. No. 2." By E. FRANKLAND, D.C.L., F.R.S. Received June 18, 1889.

Under this title I communicated to the Royal Society, in February, 1883,[†] the results of some experiments on the reactions occurring during the charging and discharging of a storage cell. I showed that no appreciable part of the storage effect was due to occluded gases, as had been previously suggested by some chemists and physicists; but that the act of charging consisted essentially in the decomposition of lead sulphate whilst the discharge was produced by the re-composition of this salt.

The establishment of these, as practically the only reactions going on in a storage cell, enabled me to prescribe a very simple method by which the charge in any cell could be ascertained; for as sulphuric acid is liberated during the charging and absorbed by the active material of the plates during discharge, the amount of charge could

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[*] ' Wiedemann, Annalen,' vol. 8, 1879, p. 98.

[†] ' Proceedings of the Royal Society,' vol. 35, p. 67.

at any time be measured by ascertaining the amount of free sulphuric acid in the cell; in other words, by simply determining the specific gravity of the electrolyte; and this method has since been very generally adopted by the users of storage batteries.

In continuing these experiments, it soon became evident that the lead sulphate formed and decomposed in the cell could not be the ordinary white sulphate hitherto known to chemists, because, in the first place, the active material of the plates always remains coloured even after discharge, and secondly, because whenever white sulphate is produced through abnormal reactions in the cell, it is afterwards decomposed only with extreme difficulty by the electric current.

In order to obtain some light upon the composition of the sulphate formed and decomposed in the cell, I have studied the action of dilute sulphuric acid upon litharge and minium, the two oxides of lead chiefly used in the construction of the plates of storage cells.

Action of Dilute Sulphuric Acid on Litharge.

Finely powdered litharge was treated with successive portions of dilute sulphuric acid until the liquid remained strongly acid after prolonged trituration. The resulting insoluble buff-coloured powder was washed with water till free from acid, and dried, first at $100°$ C. and afterwards at $150—160°$. The loss at this higher temperature was less than $0\cdot2$ per cent., and was therefore due to hygroscopic moisture.

PbO and SO_3 were then determined in the dried compound as follows :—The salt was dissolved in a small quantity of pure concentrated solution of caustic potash, and the solution, after dilution, was saturated with CO_2. (According to H. Rose, $COPbo''$ is soluble in $COKo_2$, but not in $COHoKo$.) Any excess of CO_2, which might have caused the $COPbo''$ to dissolve, was avoided by warming the liquid with the precipitate on the water-bath to a temperature at which the $COHoKo$ begins to dissociate. The liquid was then allowed to cool and to stand twelve hours before filtering. The $COPbo''$ was filtered off, converted into nitrate, and precipitated and weighed as sulphate. The sulphuric acid was determined in the filtrate from the $COPbo''$.

$1\cdot2964$ grams of the salt gave $0\cdot6647$ gram baric sulphate and $1\cdot4437$ gram plumbic sulphate.
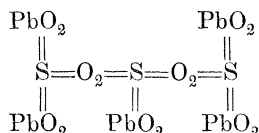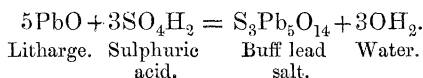
These numbers agree closely with the formula—

$$(SO_3)_3(PbO)_5,$$
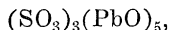
as is seen from the following comparison of calculated and experimental numbers :—

z 2

	Calculated.			Found.
$3SO_3$	240	17·71	....	17·61
$5PbO$	1115	82·29	....	81·96
	1355	100·00		99·57

These analytical results suggest the following graphic formula :—

$$\begin{array}{ccc} PbO_2 & & PbO_2 \\ \| & & \| \\ S{=}O_2{=}S{=}O_2{=}S \\ \| & \| & \| \\ PbO_2 & PbO_2 & PbO_2 \end{array}$$

The formation of this salt may be represented by the following equation :—

$$5PbO + 3SO_4H_2 = S_3Pb_5O_{14} + 3OH_2.$$

Litharge. Sulphuric   Buff lead   Water.
             acid.   salt.

Action of Dilute Sulphuric Acid on Minium.

Minium was treated with dilute sulphuric acid in exactly the same way as litharge, and the resulting brownish red compound dried, first at 100° C., and afterwards at 150—160°. The loss at this higher temperature was again less than 0·2 per cent.

PbO, SO_3, and excess of oxygen were then determined in this salt in the following manner :—The salt was first treated with concentrated hydrochloric acid in order to reduce all the lead to the monoxide stage. The resulting mixture was then dissolved in caustic potash and treated as already described. The excess of oxygen was determined by finding the loss of weight which resulted from the evolution of CO_2 when the salt was treated with oxalic acid and dilute nitric acid.
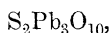
2·1136 grams of the salt gave 1·1978 grams baric sulphate and 2·2710 grams lead sulphate.

1·5110 gram treated with oxalic acid and dilute nitric acid evolved 0·0910 gram CO_2.

These numbers correspond to the following percentages :—
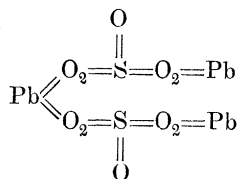
SO_3	19·46
PbO	79·08
O	1·09
	99·63

which agree with the formula—

$$S_2Pb_3O_{10},$$

as is seen from the following comparison :—

	Calculated.			Found.
S_2	64	7·57	....	7·78
Pb_3	621	73·49	....	73·41
O_{10}	160	18·94	....	18·44
	845	100·00		99·63

The composition of this salt may be represented graphically thus :—

$$Pb \Big\langle \begin{matrix} O \\ \| \\ O_2{=}S{=}O_2{=}Pb \\ O_2{=}S{=}O_2{=}Pb \\ \| \\ O \end{matrix}$$

The formation of this salt is expressed by the following equation :—

$$Pb_3O_4 + 2SO_4H_2 = S_2Pb_3O_{10} + 2OH_2.$$

Minium.   Sulphuric   Red lead   Water.
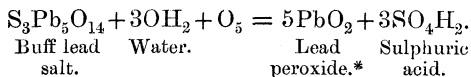acid.   salt.
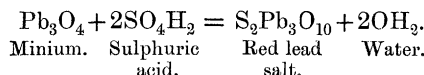
These then are the salts which constitute the original active material of storage cells when that material is formed by the admixture of sulphuric acid with litharge or minium respectively, and it is highly probable that one or the other of these salts takes part in the electrolytic processes of the storage battery. It is fortunate that these hitherto unknown salts (and not the ordinary known sulphate) are formed in the cell reactions; for, in the alternative case, lead storage batteries would be practically valueless.
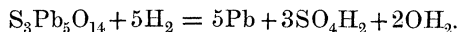
If the buff lead salt be the active material of the battery plates, then the following equations express the electrolytic reactions taking place in the cell:—
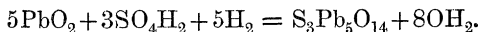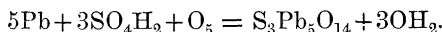
I. In charging—

(*a.*) *Positive Plates.*

$$S_3Pb_5O_{14} + 3OH_2 + O_5 = 5PbO_2 + 3SO_4H_2.$$

Buff lead   Water.   Lead   Sulphuric
salt.   peroxide.*   acid.

(*b.*) *Negative Ptates.*
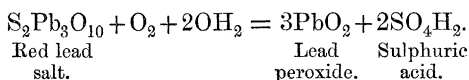
$$S_3Pb_5O_{14} + 5H_2 = 5Pb + 3SO_4H_2 + 2OH_2.$$

* Mr. Fitzgerald considers that this peroxide is hydrated.

II. In discharging—

(*a.*) *Positive Plates.*
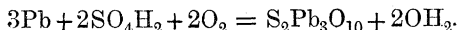
$$5PbO_2 + 3SO_4H_2 + 5H_2 = S_3Pb_5O_{14} + 8OH_2.$$

(*b.*) *Negative Plates.*

$$5Pb + 3SO_4H_2 + O_5 = S_3Pb_5O_{14} + 3OH_2.$$

If the red lead salt be the active material, then the following equations express the same electrolytic reactions:—

I. In charging—

(*a.*) *Positive Plates.*

$$S_2Pb_3O_{10} + O_2 + 2OH_2 = 3PbO_2 + 2SO_4H_2.$$
Red lead   Lead   Sulphuric
   salt.   peroxide.   acid.

(*b.*) *Negative Plates.*

$$S_2Pb_3O_{10} + 4H_2 = 3Pb + 2SO_4H_2 + 2OH_2.$$

II. In discharging—

(*a.*) *Positive Plates.*

$$3PbO_2 + 2SO_4H_2 + 2H_2 = S_2Pb_3O_{10} + 4OH_2.$$

(*b.*) *Negative Plates.*

$$3Pb + 2SO_4H_2 + 2O_2 = S_2Pb_3O_{10} + 2OH_2.$$
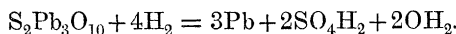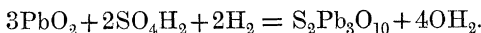
An inspection of these equations discloses, in the case of the red lead salt, a fact which has already been roughly observed in practice, viz., that only half as much active material is electrolytically decomposed on the negative as on the positive plates; whence it follows that the weight of active material on the negative plates need not exceed one-half of that upon the positive plates; for, in the decomposition of the electrolyte, equivalent quantities of oxygen and hydrogen are evolved; that is to say, two atoms of hydrogen for each atom of oxygen. But, in the decomposition of the red lead salt, four times as many atoms of hydrogen are required to reduce the salt to metallic lead as atoms of oxygen which are necessary to transform the lead of the salt into peroxide. When, however, the active material of the positive plate has once been converted into peroxide of lead, it seems probable that the red salt only is formed; at all events until the discharge at high potential is nearly completed, when there are indications of the production of the buff-coloured salt. But this is a point requiring further investigation.

I have to thank Dr. F. R. Japp, F.R.S., for his assistance in the analytical work of this investigation.